

CONDUCTIVE COMPOSITION PRECURSOR, CONDUCTIVE  
COMPOSITION, SOLID ELECTROLYTIC CAPACITOR, and THEIR  
MANUFACTURING METHOD

5

FIELD OF THE INVENTION

The present invention relates to conductive composition precursors,  
conductive compositions, solid electrolytic capacitors, and their manufacturing  
10 methods, and more particularly to conductive compositions with high  
dielectric layer repairing ability and solid electrolytic capacitors with good  
withstand voltage employing such conductive compositions.

15

BACKGROUND OF THE INVENTION

Demand for small high-capacitance capacitors with low impedance at  
high frequencies is growing in response to the increasing digitization of  
electric appliances. Conventional capacitors used at high frequencies include  
20 mica capacitors and multi-layered ceramic capacitors. Downsizing of these  
capacitors, however, is difficult to reconcile with maintenance of large  
capacity.

Typical large-capacitance capacitors are electrolytic capacitors such as  
aluminum electrolytic capacitors and aluminum or tantalum solid electrolytic  
25 capacitors. The extremely thin anodized layer which becomes the dielectric  
of these capacitors allows them to achieve large capacitance. On the other  
hand, thin anodized layers are fragile, and thus these capacitors require  
electrolytic substances to allow them to repair themselves.

For example, in aluminum electrolytic capacitors, an etched positive  
30 electrode and aluminum foil forming the negative electrode are wound  
together, providing a separator in between, and the separator is impregnated

with liquid electrolyte. This liquid electrolyte has ion conductivity and large specific resistance, resulting in large losses which significantly degrade the frequency characteristics as well as the impedance and temperature characteristics. Moreover, leakage of liquid and evaporation of solvent are  
5 inevitable, resulting in reduced capacitance and increased loss as time passes. Solid tantalum electrolytic capacitors use manganese oxides as their electrolyte for improved temperature characteristics and reduced secular change of capacity and loss. However, the relatively high specific resistance of manganese oxide results in poor impedance frequency characteristics  
10 compared to multi-layered ceramic capacitors and film capacitors. To counter this disadvantage, solid aluminum and tantalum electrolytic capacitors with high electric conductivity employing conjugated double bond conductive polymer are proposed.

In general, conjugated double bond conductive polymers, typically  
15 poly-aniline and poly-thiophene, are prepared by chemical oxidative polymerization and electro-polymerization. Application of electro-polymerization puts a limit on mass production because conductive polymer are formed on an electrode in a film. In contrast, application of chemical oxidative polymerization is free from such restrictions,  
20 and allows a large volume of conductive polymer to be relatively easily produced by reacting a monomer using an oxidizing agent. In order to use such conductive polymer as the negative electrode conductive layer of a solid electrolytic capacitor, it is important to provide the conductive polymer with high environmental stability and high dielectric layer repairing  
25 ability.

The conductive polymer consists of polymer as a main component and dopant. Selection of dopant anionic material or introduction of an appropriate substitute group for monomer has conventionally been applied to improve environmental stability of the conductive polymer.  
30 In particular, a number of studies have been carried out on the use of thiophene as the monomer by introducing the ethylene dioxy group to its  $\beta$ ,  $\beta'$

positions (3, 4 positions) for creating a conductive composition with high environmental stability.

It is generally thought that the dielectric layer of the conductive polymer used in the solid electrolytic capacitor is self-repaired by the change  
5 of the conductive polymer to insulating polymer as a result of the joule heat generated by the current flowing the dielectric layer defect portion. Conventionally, the dielectric layer formed by anodization is thickened to achieve a solid electrolytic capacitor with high withstand voltage, using conductive polymer for the negative electrode conductive layer. In other  
10 words, the anodization voltage is often increased to thicken the dielectric layer. Another approach is the use of anionic compounds which have high dielectric layer repairing ability as dopants for in-situ formation of the negative electrode conductive layer consisting of conductive polymer.

Still another approach is to carry out in-situ polymerization in the  
15 presence of phenol derivatives to form a negative electrode conductive layer consisting of conductive polymer to provide high dielectric layer repairing ability and thus to achieve a capacitor with high withstand voltage. However, the strategy of increasing the anodization voltage during the formation of the dielectric layer to allow a sufficient margin against the  
20 applied voltage with the aim of securing a high withstand voltage thickens the dielectric layer in proportion to the rated voltage, causing the undesirable result of reducing the capacitance of the capacitor.

In addition, it is difficult to achieve both sufficiently high environmental stability, particularly high heat resistance in the air, and high  
25 dielectric layer repairing ability at the same time using a single dopant, although the properties of the polypyrrole are changeable by types of dopant used.

Accordingly, several dopants are often used in some approaches, but it is still difficult to achieve a conductive polymer with high heat resistance and  
30 high layer repairing ability because doping ability varies among dopants and the control of individual doping ratio is difficult.

The use of additives for improving the layer repairing ability has also been studied, but most of the additives that are added to the polymerizing solution for in-situ polymerization are removed during the rinsing for removal of polymerization residue, and thus sufficiently high layer repairing effects are not achieved.

The repairing ability of conductive polymer using anionic materials, which have a high anodization layer repairing ability, as dopants, still confers a low level of repairing ability combined with low withstand voltage.

However, there is strong market demand for solid electrolytic capacitors using conductive polymer with withstand voltages the same with those of general electrolytic capacitors.

## SUMMARY OF THE INVENTION

The present invention aims to offer conductive composition precursors and a method for manufacturing conductive compositions having high withstand voltage and high layer repairing ability for overcoming the disadvantages of the prior art.

Moreover, the present invention provides a method of manufacture solid electrolytic capacitors showing high withstand voltage, heat resistance, and moisture resistance, utilizing the features of the conductive polymer of the present invention.

The present invention provides, conductive composition precursor made by dispersing or dissolving an additive having high dielectric layer repairing ability into a conductive polymer solution in which soluble conductive polymer is dissolved or into a conductive polymer dispersion into which conductive polymer particles are dispersed;

conductive composition achieved by removing the medium or solvent; and

a method of manufacturing a solid electrolytic capacitor using the conductive composition of the present invention.

The present invention uses at least one additive selected from the group of "phosphoric acid or esters of phosphoric acid," "phenol or phenol  
5 derivatives," "nitrobenzene derivatives," "alkyl naphthalene sulfonic acid anion," "fluorocarbon surface active agents," or "fluorocarbon surface active agents and binders."

The present invention also applies at least one coupling agent selected from the group of: silane coupling agent, titanium coupling agent, borane  
10 coupling agent, or aluminum coupling agent to the surface of the anodized layer for providing an extremely thin insulating layer between the anodized layer and conductive polymer. Provision of a coupling agent layer and a layer made of a surface active agent with strong affinity to this coupling agent  
15 between the anodized layer and conductive polymer prevents direct contact between the anodized layer defect portion and the conductive polymer. Accordingly, the withstand voltage is improved by preventing the electrical breakdown of conductive polymer by the current from the dielectric layer damaged portion.

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## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a sectional view of a configuration of a capacitor in accordance with an exemplary embodiment of the present invention,

25 Fig. 2 is a perspective view of the capacitor in accordance with the exemplary embodiment of the present invention,

Fig. 3A illustrates a configuration of an electrode foil in accordance with the exemplary embodiment of the present invention,

Fig. 3B is a sectional view of a configuration of a capacitor in  
30 accordance with another exemplary embodiment of the present invention,

Fig. 4 illustrates a configuration of an electrode foil in accordance

with another exemplary embodiment of the present invention, and

Fig. 5 is a sectional view of a configuration of a capacitor in accordance with another exemplary embodiment of the present invention.

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### Description of the PREFERRED EMBODIMENT

Exemplary embodiments of the present invention are detailed next.

#### 10 First exemplary embodiment

Whether the conductive polymer used for the present invention takes the form of particles dispersed in the medium or an intrinsic solution is a matter of controversy.

For convenience, in the following explanation of the invention, a  
15 'conductive polymer solution' refers to both of the dispersion and solution. In the same way, for convenience, additives are also referred to as being "dissolved", including those dispersed in a colloidal state.

A series of methods for manufacturing the conductive polymer solution used in the present invention are already disclosed, and thus the  
20 applicable conductive polymer solution can be easily manufactured using these disclosed methods.

For example, methods of manufacturing poly-pyrroles are disclosed in Japanese Patent Laid-open Publication No. H6-206986 and by E.E. Havinga et al, Chemistry of Materials (American Chemical Society), 1 (6), pp650 (1989).

25 F.Yonas et al, Synthetic Metals(Elsevia Press), 85, 1397 and Hotta et al, ibid, 26, 267 disclose the methods of manufacturing poly-thiophenes.

U.S. Patent No. 5232631 and Shimizu et al, Synthetic Metals, 85, 1337 disclose the methods of manufacturing polyaniline solution.

Mitsubishi Rayon Co.Ltd. sells poly-aniline solution under the trade  
30 name "Aquasave."

[The present invention provides conductive composition precursor by]

The present invention provides conductive composition precursor by adding at least one of "phosphoric acid or esters of phosphoric acid," "phenol or phenol derivatives," "nitrobenzene derivatives," "alkyl naphthalene sulfonic acid anion," "fluorocarbon surface active agent," or "fluorocarbon surface  
5 active agent and binder" to a conductive polymer solution.

Conductive composition can be manufactured by removing solvent or dispersing medium (hereafter referred to as medium) from the above precursor.

As known due to the frequent use of phosphoric acid or esters of phosphoric acid to form the dielectric layer of aluminum electrolytic capacitors and tantalum electrolytic capacitors, phosphoric acid or esters of  
10 phosphoric acid are known to form a barrier type oxide layer.

The present invention allows the use of salts of phosphoric acids in which at least one active hydrogen remains, as well as ortho-phosphoric acid.

As for phosphoric acid ester compounds, any compounds in which at  
15 least one active hydrogen remains and is uniformly dispersed in the conductive polymer solution may be used. However, the use of esters of alkyl phosphoric acid including 3 to 8 carbons are preferable.

Anodized layer formation may occur to a sufficient degree in the presence of a small amount of absorbed water supplied from the air when  
20 phosphoric acid ester compounds are added. Accordingly, the use of conductive composition of the present invention as a negative electrode conductive layer makes it possible to achieve a capacitor with improved withstand voltage due to its high dielectric layer repairing ability.

The second group of the present invention is precursors in which  
25 phenol or phenol derivatives, or benzene derivatives having nitro groups are added to a conductive polymer solution. Conductive composition precursor made of this group makes it possible to improve the repairing ability of a dielectric layer made of valve metal anodized film.

It is known that the spark discharge initiation voltage rises and  
30 withstand voltage improves as a result of addition of p-nitro-phenol or p-nitro-benzoic acid to the electrolytic solution. The inventor has found that when a

solid electrolytic capacitor using conductive composition as the negative electrode conductive layer to which p-nitro-phenol and p-nitro-benzoic acid are added, it achieves high withstand voltage compared with the same kind of capacitor without ing these substances.

5           Phenol derivatives suitable for the present invention include phenol derivatives having electron-attracting substitution groups as well as p-nitro-phenol.

As for benzene derivatives having a nitro group, p-nitro-benzoic acid and nitro-benzyl alcohol as well as nitrobenzene are preferable.

10           Poly-pyrrole or its derivatives, poly-thiophene or its derivatives, and poly-aniline or its derivatives are preferable as conductive polymer solutions for adding these additives.

Conductive polymers containing dopant may be used as the above conductive polymers, and undoped polymers may also be used if they are  
15 post-doped to become conductive.

The third group of the present invention comprises solutions to which alkyl naphthalene sulfonic-acid anion is added after preparing a conductive polymer solution. The conductive composition precursor of the above composition improves the repairing ability of the dielectric layer consisting of  
20 a valve metal oxide. Free acids, sodium salts, or ammonium salts may be added as alkyl naphthalene sulfonic acid anions. An alkyl group having total carbon number of 3 or above can be used as the alkyl group.

A conductive composition layer can be manufactured by removing medium from the conductive composition precursor.

25           Alkyl naphthalene sulfonic acid or salts of alkyl naphthalene sulfonic acid contained in the conductive composition layer prevent damage of the dielectric layer, which is caused by small volume anion such as para-toluene sulfonic acid anion or naphthalene sulfonic acid anion. Therefore, if an oxidizing agent containing salts of para-toluene sulfonate or naphthalene  
30 sulfonate is used for manufacturing a conductive polymer layer on the conductive composition, a solid electrolytic capacitor with low leak current,



and high heat and moisture resistances and high capacitance obtaining rate is achievable. The capacitance obtaining rate refers to the ratio of static capacitance in the finished solid electrolytic capacitor compared to the static capacitance of a capacitor element measured in an electrolytic solution.

5 Alkyl naphthalene sulfonic acid anion has high repairing ability, so no large current flows during re-anodization, thus preventing the decomposition of the conductive polymer layer. Accordingly, a solid electrolytic capacitor with low leak current is obtained without degrading dissipation factor and impedance.

10 If the surface of the valve metal is anodized using an anodizing solution containing alkyl naphthalene sulfonic acid anion, the alkyl naphthalene sulfonic acid anion is included near the surface of the dielectric layer. Alkyl naphthalene sulfonic acid anion included in or present near the surface of the dielectric layer suppress damage of the dielectric layer caused  
15 by small volume anions, such as para-toluene sulfonic acid anion.

As conductive polymers used in the conductive polymer layer, polypyrrole, polythiophene, polyaniline or their derivatives are preferably used.

In the fourth group of the present invention, fluorocarbon surface active agents or fluorocarbon surface active agent and binders are added to a  
20 conductive polymer solution. Addition of fluorocarbon surface active agent reduces the surface tension of the solution, and provides a conductive composition precursor with high coverage. Moreover, addition of a fluorocarbon surface active agent and binder, which becomes an insulating material after the medium is removed, provides a conductive composition  
25 precursor with high withstand voltage.

As for the fluorocarbon surface active agent, anionic, nonionic, amphoteric, or cationic surface active agents may be used. For example, anionic surface active agents include perfluoroalkyl carbonate and perfluoroalkyl phosphoric acid ester. Nonionic surface active agents include  
30 perfluoroalkyl amine oxide and perfluoroalkyl ethylene oxide adduct. Amphoteric surface active agents include perfluoroalkyl betaine. Cationic

surface active agents include perfluoroalkyl trimethyl ammonium salts.

As for binder, polymers which dissolve or disperse in the medium of the conductive polymer solution may be used. These include polyvinyl pyrrolidone, polyvinyl alcohol, water soluble polyester, water soluble acrylic  
5 resin, carboxymethyl cellulose, salts of polyvinyl sulfonic acids, and salts of polystyrene sulfonic acid.

As for fluorocarbon surface active agents used together with binder, those having a perfluoroalkyl group are suitable.

The solid electrolytic capacitor of the present invention forms a  
10 negative electrode conductive layer by removing the medium after applying the conductive composition precursor, to which the above additives are added, on the surface of the capacitor electrode having the dielectric layer, using an appropriate method.

Phosphoric acid or esters of phosphoric acid, phenol derivatives, nitro  
15 compounds, alkyl sulfonic acid ion, fluorocarbon surface active agents, or fluorocarbon surface active agents and binders as additives allow a solid electrolytic capacitor with high withstand voltage to be achieved.

Other conductive polymer layers may be laminated on the initial conductive composition layer by in situ polymerization as the negative  
20 electrode conductive layer, as well as the use of a single conductive composition layer obtained from the above conductive composition precursor.

Methods for in situ polymerization include electro-polymerization and chemical polymerization. Poly-pyrrole or its derivatives, poly-thiophene or its derivatives, or poly-aniline or its derivatives are preferably used as  
25 conductive polymers.

Specific examples are described below.

(Example 1)

Example 1 is described with reference to Fig. 1.

30 First, poly-pyrrole solution is prepared using the method disclosed in Chemistry of Materials (American Chemical Society), 1 (6), pp650 (1989).

Conductive composition precursor containing poly-pyrrole, ortho-phosphoric acid, and medium is prepared by adding 0.01% of ortho-phosphoric acid to this poly-pyrrole solution.

The precursor is a smooth liquid similar to the solution without ortho-phosphoric acid. It also enables the creation of a conductive composition layer equivalent to that without additive when the precursor is applied to the substrate and the medium is then dried and removed.

Next, as shown in Fig. 1, an aluminum strip 1 of 99.99% purity and dimensions of 10 x 30 x 0.5 mm is prepared. After electrolytic polishing of aluminum strip 1 in sodium hydroxide solution, the strip is dipped in 3 % ammonium adipate solution to a depth of approximately 20 mm, and voltage of 35 V is applied for 30 minutes at 70 °C to form anodized film 2.

The conductive composition precursor containing polypyrrole, ortho-phosphoric acid, and medium is applied in a 7 mm diameter circle on one side of the aluminum strip, where anodized film is formed. The strip is then air-dried at room temperature, and heated for 10 minutes at 105 °C to form conductive composition layer 3 consisting of poly-pyrrole and ortho-phosphoric acid.

Then, colloidal graphite 4 and silver paint 5 are sequentially applied to conductive composition layer 3. A positive electrode lead is attached to a portion where the anodized film is not formed and a negative electrode lead is attached to the silver paint layer to form the capacitor. Capacitance is measured at 120 Hz.

Furthermore, a voltage is applied between both electrodes in the forward direction at an interval of 0.5 V to identify the voltage causing electrical breakdown. The results are shown in Table 1.

#### (Comparative example 1)

For comparison, a capacitor without added ortho-phosphoric acid is manufactured in Example 1 as Comparative example 1. Capacitance and electrical breakdown voltage of this capacitor are evaluated, in the same way

as in Example 1, and the results are shown in Table 1.

Comparing the results shown in Table 1, Example 1 and Comparative example 1 both have almost the same capacitance. However, it is apparent that the capacitor in Example 1 has a higher withstand voltage, demonstrating  
5 that the present invention has better effect.

(Example 2)

Example 2 shows the effects of addition of (A) n-propyl phosphoric acid, (B) isopropyl phosphoric acid, (C) n-butyl phosphoric acid, or (D) n-  
10 hexyl phosphoric acid, instead of ortho-phosphoric acid as seen in Example 1. Other conditions are the same as those in Example 1 for preparing conductive composition precursor.

These precursors are also smooth liquid similar to those containing no additives. A conductive composition layer identical to that with no additives  
15 is also provided by applying these precursors to a substrate, and drying and removing the medium. A capacitor is manufactured in the same way as that in Example 1 using each of these precursors, and the same evaluations as those in Example 1 are implemented.

The results are shown in Table 1. It is apparent that all the  
20 capacitors in Example 2 have a higher withstand voltage than that in Comparative example 1, demonstrating the advantageous effect of the present invention.

(Example 3)

25 Example 3 shows the effects of addition of (A) n-nitro phenol, (B) m-nitro phenol, or (C) n-cyano phenol, instead of ortho-phosphoric acid as seen in Example 1. Other conditions are the same as those in Example 1 for preparing conductive composition precursor.

These precursors are also smooth liquid similar to those containing no  
30 additives. A conductive composition film identical to that with no additives is also provided by applying these precursors to a substrate, and drying and

removing the medium. A capacitor is manufactured in the same way as that in Example 1 using these precursors, and the same evaluations as those in Example 1 are implemented.

The results are shown in Table 1. It is apparent that all the capacitors in Example 3 have a higher withstand voltage than that in Comparative example 1, demonstrating the advantageous effect of the present invention.

#### (Example 4)

Example 4 shows the effects of addition of (A) p-nitro benzoic acid, (B) m-nitro benzoic acid, or (C) p-nitro benzyl alcohol, instead of ortho-phosphoric acid as seen in Example 1. Other conditions are the same as those in Example 1 for preparing conductive composition precursor.

These precursors are also smooth liquid similar to those containing no additives. A conductive composition layer identical to that with no additives is also provided by applying these precursors to a substrate, and drying and removing the medium. A capacitor is manufactured in the same way as that in Example 1 using each of these precursors, and capacitance and withstand voltage are evaluated.

The results are shown in Table 1. It is apparent that all the capacitors in Example 4 have a higher withstand voltage than that in Comparative example 1, demonstrating the advantageous effect of the present invention.

#### (Example 5)

An aqueous dispersion containing about 0.4 weight % colloidal poly ( 3,4-ethylene dioxy thiophene ) particles was first prepared by the method disclosed in Synthetic Metals (Elsevia Press), 85, pp1397. In the present example, above aqueous dispersion was used instead of poly-pyrrole solution as seen in Example 1. Other conditions are the same as those in Example 1 for preparing conductive composition precursor.

This precursor is also smooth liquid similar to those containing no additives. A conductive composition layer identical to that with no additives

is also provided by applying this precursor to a substrate, and drying and removing the medium. A capacitor is manufactured in the same way as that in Example 1 using this precursor, and capacitance and withstand voltage are evaluated. The results are shown in Table 1.

5

(Comparative example 2)

For comparison, a capacitor without added ortho-phosphoric acid is manufactured in Example 5 as Comparative example 2. Capacitance and electrical breakdown voltage of this capacitor are evaluated, and the results are shown in Table 1.

10

Comparing the results shown in Table 1, Example 5 and Comparative example 2 both have almost the same capacitance. However, it is apparent that the capacitor in Example 5 has a higher withstand voltage, demonstrating that the present invention has better effect.

15

(Example 6)

Example 6 shows the effects of addition of (A) n-propyl phosphoric acid, (B) isopropyl phosphoric acid, (C) n-butyl phosphoric acid, or (D) n-hexyl phosphoric acid, instead of ortho-phosphoric acid as seen in Example 5 for preparing conductive composition precursor.

20

These precursors are also smooth liquid similar to those containing no additives. A conductive composition later identical to that with no additives is also provided by applying these precursors to a substrate, and drying and removing the medium. A capacitor is manufactured in the same way as that in Example 1 using each of these precursors, and the same evaluations as those in Example 1 are implemented.

25

The results are shown in Table 1. It is apparent that all the capacitors in Example 6 have a higher withstand voltage than that in Comparative example 2, demonstrating the advantageous effect of the present invention.

30

(Example 7)

Example 7 shows the effects of addition of (A) p-nitro phenol, (B) m-nitro phenol, or (C) n-cyano phenol, instead of ortho-phosphoric acid as seen in Example 5 for manufacturing conductive composition precursor.

These precursors are also smooth liquid similar to those containing no additives. A conductive composition layer identical to that with no additives is also achieved by applying these precursors to a substrate, and drying and removing the medium. A capacitor is manufactured in the same way as that in Example 1 using these precursors, and capacitance and withstand voltage are evaluated.

Table 1 shows the results. It is apparent that all the capacitors in Example 6 have a higher withstand voltage than that in Comparison 2, demonstrating the advantageous effect of the present invention.

(Example 8)

Example 8 shows the effects of addition of (A) p-nitro benzoic acid, (B) m-nitro benzoic acid, or (C) p-nitro benzylic alcohol, instead of orthophosphoric acid as seen in Example 5.

These precursors are also smooth liquid similar to those containing no additives. A conductive composition film identical to that with no additives is also provided by applying these precursors to a substrate, and drying and removing the medium. A capacitor is manufactured in the same way as that in Example 1 using each of these precursors, and capacitance and withstand voltage are evaluated.

The results are shown in Table 1. It is apparent that all the capacitors in Example 8 have a higher withstand voltage than that in Comparative example 2, demonstrating the advantageous effect of the present invention.

(Example 9)

Example 9 uses metacresol solution of poly-aniline prepared by the method disclosed in U.S. Patent No. 5232631.

The conductive composition precursor is manufactured in the same way as that in Example 1 except for the use of polyaniline metacresol solution instead

of poly-pyrrole solution. This precursor also was smooth liquid similar to those containing no additives. A conductive composition layer identical to that with no additives is also provided by applying this precursor to a substrate, and drying and removing the medium. A capacitor is manufactured in the  
5 same way as that in Example 1 using this precursor, and capacitance and withstand voltage are evaluated. The results was shown in Table 1.

(Comparative example 3)

For comparison, a capacitor without added ortho-phosphoric acid is  
10 manufactured in Example 9 as Comparative example 3. Capacitance and electrical breakdown voltage of this capacitor are evaluated, and the results are shown in Table 1.

Comparing the results shown in Table 1, Example 9 and Comparative  
example 3 both have almost the same capacitance. However, it is apparent  
15 that the capacitor in Example 9 has a higher withstand voltage, demonstrating that the present invention has better effect.

(Example 10)

Example 10 shows the effects of addition of (A) n-propyl phosphoric  
20 acid, (B) isopropyl phosphoric acid, (C) n-butyl phosphoric acid, or (D) n-hexyl phosphoric acid, instead of ortho-phosphoric acid as seen in Example 9 for preparing conductive composition precursor.

These precursors are also smooth liquid similar to those containing no additives. A conductive composition layer identical to that with no additives  
25 is also provided by applying these precursors to a substrate, and drying and removing the medium. A capacitor is manufactured in the same way as that in Example 1 using each of these precursors, and the same evaluations as those in Example 1 are implemented.

The results are shown in Table 1. It is apparent that all the  
30 capacitors in Example 10 have a higher withstand voltage than that in Comparative example 3, demonstrating the advantageous effect of the present



invention.

(Example 11)

Example 11 shows the effects of addition of (A) n-nitro phenol, (B) m-  
5 nitro phenol, or (C) p-cyano phenol, instead of ortho-phosphoric acid as seen  
in Example 9 for preparing conductive composition precursor.

These precursors are also smooth liquid similar to those containing no  
additives. A conductive composition layer identical to that with no additives  
is also achieved by applying these precursors to a substrate, and drying and  
10 removing the medium. A capacitor is manufactured in the same way as that  
in Example 1 using these precursors, and capacitance and withstand voltage  
are evaluated.

The results are shown in Table 1. It is apparent that all the  
capacitors in Example 11 have a higher withstand voltage than that in  
15 Comparative example 3, demonstrating the advantageous effect of the present  
invention.

(Example 12)

Example 4 shows the effects of addition of (A) p-nitro benzoic acid,  
20 (B) m-nitro benzoic acid, or (C) p-nitro benzyl alcohol, instead of ortho-  
phosphoric acid as seen in Example 9 for preparing conductive composition  
precursor.

These precursors are also smooth liquid similar to those containing no  
additives. A conductive composition layer identical to that with no additives  
25 is also provided by applying these precursors to a substrate, and drying and  
removing the medium. A capacitor is manufactured in the same way as that  
in Example 1 using each of these precursors, and capacitance and withstand  
voltage are evaluated.

The results are shown in Table 1. It is apparent that all the capacitors  
30 in Example 12 have a higher withstand voltage than that in Comparative  
example 3, demonstrating the advantageous effect of the present invention.

(Example 13)

Example 13 uses a tantalum strip with a purity of 99.99% and the same dimensions as the aluminum strip in Example 1. A voltage of 35 V is applied to the tantalum strip for an hour using 0.5% phosphoric acid solution at 90 °C to form an anodized layer. Other conditions are the same as those in Example 1 for manufacturing the capacitor. The capacitance and withstand voltage of this capacitor are evaluated in the same way as in Example 1. The results are shown in Table 1.

(Comparative example 4)

For comparison, a capacitor without added ortho-phosphoric acid is manufactured in Example 13 as Comparative example 4. Capacitance and electrical breakdown voltage of this capacitor are evaluated, and the results are shown in Table 1.

Comparing the results shown in Table 1, Example 13 and Comparative example 4 both have almost the same capacitance. However, it is apparent that the capacitor in Example 13 has a higher withstand voltage, demonstrating that the present invention has better effect.

(Example 14)

An anodized layer is formed under the same conditions as those used in Example 1, on 0.1 mm thick highly-etched aluminum foil. This etched aluminum foil is then cut into a 2.3 x 155 mm piece, and positive electrode lead 12 is attached to prepare capacitor positive electrode foil 11. Then, 0.05 mm thick highly-etched aluminum is cut into 2.3 x 180 mm piece, and negative electrode lead 14 is attached to prepare negative electrode foil 13. As shown in Fig. 2, both foils are wound together with a 2.5 x 220 mm separator 15 made of Manila hemp to manufacture a wound aluminum electrolytic capacitor element. Then, adhesive tape 16 is applied to one end of this capacitor element, and anodization is implemented again under the same conditions as Example 1. The capacitance of this capacitor element is

125  $\mu$ F.

This capacitor element is impregnated with the conductive composition precursor manufactured in Example 1, and then dried to form the conductive composition layer.

5        Then, 10 g of methanol solution containing 40 weight % of iron (II) salt of naphthalene sulfonic acid and 1.6 g of pyrrole monomer are mixed at minus 30 °C. The capacitor element kept at the same temperature is impregnated with the above mixed solution to laminate a poly-pyrrole layer on the conductive composition layer. The capacitor is evaluated after the  
10        polymerization residue is cleaned and dried. Table 1 shows the results.

(Comparative example 5)

For comparison, a capacitor in which the conductive composition layer is formed using the poly-pyrrole solution without added ortho-phosphoric acid  
15        is manufactured in Example 14 as Comparative example 5. This capacitor is evaluated, and the results are shown in Table 1.

Comparing the results shown in Table 1, the capacitor in Example 14 has a higher withstand voltage, demonstrating that the present invention has better effect.

20        In the above examples, only the use of aluminum, tantalum, and etched aluminum foil which have smooth surfaces is described. It is apparent, however, that porous tantalum sintered body is also applicable. The present invention is thus not limited by the shape of the electrode.

The above examples also only refer to the use of aluminum and  
25        tantalum as the valve metal. It is apparent that other valve metals such as niobium, titanium, and zirconium may be used as electrodes of the capacitor of the present invention. Inter metallic compounds of valve metals are also applicable to the electrode of the present invention.

Example 14 describes only the case of forming the negative electrode  
30        conductive layer by laminating a poly-pyrrole layer obtained by in-situ chemical polymerization on the conductive composition of poly-pyrrole.

Other conductive polymer layers may also be laminated. The conductive polymer may also be laminated such as by electro-polymerization instead of chemical polymerization. The combination of conductive polymer in the present invention is thus not limited to types and polymerizing methods of  
5 conductive polymer.

Example 14 describes only the case of forming conductive composition using conductive composition precursor mainly consisting of poly-pyrrole and additive. It is apparent that conductive composition precursors containing other conductive polymers and additives are applicable.

10 The above Examples only refer to conductive composition precursor containing only soluble conductive polymer or conductive polymer particles, additives for improving the dielectric layer-forming capability and dispersing medium. However, other additives for improving adhesion to the metal foil or the conductive composition layer formed on the metal foil or the stability of  
15 the dispersion may also be used.

A range of additives may also be added to the medium for polymerization.

The conductive composition may also be formed as the negative electrode conductive layer by repeated application or immersion of the  
20 conductive composition precursor instead of laminating the conductive polymer layer by in-situ polymerization.

Other poly-thiophene derivatives in addition to conductive composition precursor made of colloidal polyethylene dioxy thiophene particles and water may be used. Other materials may also be added to  
25 improve the film forming capability such as by changing the adhesion or wettability to the dielectric surface or separator.

The present invention thus facilitates the production of conductive composition precursor and conductive composition with high dielectric layer repairing ability in electrolytic capacitors.

30 Moreover, the present invention has the desirable effect of improving the withstand voltage of the capacitor because the negative electrode

conductive layer made of conductive composition with high dielectric layer forming capability is formed by applying or immersing the conductive composition precursors of the present invention on the surface of the capacitor electrode.

5

(Example 15)

As in Example 5, aqueous dispersion composition containing about 0.4 weight % of colloidal poly (3,4-ethylene dioxy thiophene) particles is prepared. The conductive composition precursor is manufactured by adding  
10 0.2 weight % of perfluoro alkyl phosphoric acid ester which is a fluorocarbon surface active agent to this aqueous dispersion composition.

This conductive composition precursor is also smooth liquid similar to those containing no fluorocarbon surface active agent. A conductive composition film identical to that with no fluorocarbon surface active agent is  
15 also provided by applying this precursor to a substrate, and drying and removing the medium.

Next, as shown in Fig. 1, aluminum strip 1 of 99.99% purity and dimensions of 10 x 30 x 0.5 mm is prepared. After electrolytic polishing of aluminum strip 1 in sodium hydroxide solution, the strip is dipped in 3 %  
20 ammonium adipate solution to a depth of approximately 20 mm, and voltage of 35 V is applied for 30 minutes at 70 °C to form anodized layer 2.

The above conductive composition precursor is applied in a 7 mm diameter circle on one side of the aluminum strip where anodized film is formed. The strip is heated at 50°C for 60 minutes, and then at 130°C for 20  
25 minutes to form conductive composition layer 3 consisting of poly (3,4-ethylene dioxy thiophene) and fluorocarbon surface active agent.

Then, colloidal graphite layer 4 and silver paint layer 5 are sequentially applied to conductive composition layer 3 to form the capacitor.

Positive electrode lead 12 is attached to a portion where the anodized  
30 layer is not formed on aluminum strip 1 and a negative electrode lead is attached to silver paint layer 5. Capacitance is measured at 120 Hz.

Furthermore, a voltage is applied between both electrodes in the forward direction at an interval of 0.5 V to identify the voltage causing electrical breakdown. Table 1 shows the results.

5 (Comparative example 6)

For comparison, a capacitor without added fluorocarbon surface active agent is manufactured in Example 15 as Comparative example 6.

Capacitance and electrical breakdown voltage of this capacitor are evaluated, and the results are shown in Table 1.

10 Comparing the results shown in Table 1, Example 15 and Comparative example 6 both have almost the same capacitance. However, it is apparent that the capacitor in Example 15 has a higher withstand voltage, demonstrating that the present invention has better effect.

15 (Example 16)

Example 16 shows the effects of addition of (A) salt of perfluoro alkyl carboxylic acid, (B) perfluoro alkyl amine oxide, (C) perfluoro alkyl ethylene oxide adduct, (D) perfluoro alkyl betaine, or (E) perfluoro alkyl trimethyl ammonium salt, instead of perfluoro alkyl phosphoric acid ester as seen in

20 Example 15.

These precursors are also smooth liquid similar to those containing no additives. A conductive composition layer identical to that with no additives is also provided by applying these precursors to a substrate, and drying and removing the medium. A capacitor is manufactured in the same way as that

25 in Example 15 using each of these precursors, and the same evaluations as those in Example 15 are implemented.

Table 1 shows the results. It is apparent that all the capacitors in Example 16 have a higher withstand voltage than that in Comparative example 6, demonstrating the advantageous effect of the present invention.

30

(Example 17)

First, about 1 weight % poly-pyrrole solution is prepared using the method disclosed in Chemistry of Materials (American Chemical Society), 1 (6), pp 650 (1989).

Example 17 shows the effects of addition of poly-pyrrole solution,  
5 instead of aqueous dispersion composition as seen in Example 15. Other conditions are the same as those in Example 15 for preparing conductive composition precursor.

This conductive composition precursor is also smooth liquid similar to those containing no fluorocarbon surface active agent. A conductive  
10 composition layer identical to that with no fluorocarbon surface active agent is also provided by applying this precursor to a substrate, and drying and removing the medium.

A capacitor is manufactured in the same way as that in Example 15 using this conductive composition precursor, and capacitance and withstand  
15 voltage are evaluated in the same way as in Example 15. Table 1 shows the results.

(Comparative example 7)

For comparison, a capacitor without added fluorocarbon surface active  
20 agent is manufactured in Example 17 as Comparative example 8. Capacitance and electrical breakdown voltage of this capacitor are evaluated in the same way as in Example 15, and the results are shown in Table 1.

Comparing the results shown in Table 1, Example 17 and Comparative  
example 7 both have almost the same capacitance. However, it is apparent  
25 that the capacitor in Example 17 has a higher withstand voltage, demonstrating that the present invention has better effect.

(Example 18)

First, sulfonated poly-aniline aqueous solution composition in which  
30 about 5 weight % of soluble conductive polymer is dissolved is prepared by the method disclosed in Synthetic Metals, 85, pp 1337.

Example 18 shows the effects of using poly-aniline aqueous solution, instead of aqueous dispersion composition as seen in Example 15. Other conditions are the same as those in Example 15 for preparing conductive composition precursor.

5           This conductive composition precursor is also smooth liquid similar to those containing no fluorocarbon surface active agent. A conductive composition layer identical to that with no additive is also provided by applying this precursor to a substrate, and drying and removing the medium.

10           A capacitor is manufactured in the same way as that in Example 15 using this conductive composition precursor, and capacitance and withstand voltage are evaluated in the same way as those in Example 15. Table 1 shows the results.

(Comparative example 8)

15           For comparison, a capacitor without added fluorocarbon surface active agent is manufactured in Example 18 as Comparative example 8. Capacitance and electrical breakdown voltage of this capacitor are evaluated in the same way as in Example 15, and the results are shown in Table 1.

20           Comparing the results shown in Table 1, Example 18 and Comparative example 8 both have almost the same capacitance. However, it is apparent that the capacitor in Example 18 has a higher withstand voltage, demonstrating that the present invention has better effect.

(Example 19)

25           In Example 19, about 10 weight % of water soluble acrylic resin is added as a binder to the conductive composition precursor in Example 15 for manufacturing conductive composition precursor. This conductive composition precursor is smooth liquid similar to those containing no additives. A conductive composition layer identical to that with no  
30           fluorocarbon surface active agent and binder is also provided by applying this precursor to a substrate, and drying and removing the medium.



A capacitor is manufactured in the same way as that in Example 15 using this conductive composition precursor, and capacitance and withstand voltage are evaluated as those in Example 15.

Table 1 shows the results. It is apparent that the capacitor in Example 19 has a higher withstand voltage than that in Comparison 6, demonstrating the advantageous effect of the present invention.

(Example 20)

Example 20 shows the effects of addition of (A) polyvinyl pyrrolidone, (B) polyvinyl alcohol, (C) water soluble polyester, or (D) carboxymethyl cellulose, instead of water soluble acrylic resin as seen in Example 19 for preparing conductive composition precursor.

These precursors are also smooth liquid similar to those containing no additives. A conductive composition film identical to that with no additives is also achieved by applying these precursors to a substrate, and drying and removing the medium.

A capacitor is manufactured in the same way as that in Example 15 using each of these conductive composition precursors, and the same evaluations as those in Example 15 are implemented.

Table 1 shows the results. It is apparent that all the capacitors in Example 16 have a higher withstand voltage than that in Comparative example 6, demonstrating the advantageous effect of the present invention.

(Example 21)

An anodized layer is formed by immersing a 0.1 mm thick highly-etched aluminum foil into 3% ammonium adipate solution, and applying voltage of 80V at 70 °C for 30 minutes. After forming the anodized layer, the etched aluminum strip is cut into a 2.3 x 155 mm piece, and positive electrode lead 12 is attached to prepare capacitor positive electrode foil 11. Then, 0.05 mm thick highly-etched aluminum is cut into a 2.3 x 180 mm piece, and negative electrode lead 14 is attached to prepare negative electrode foil 13.

As shown in Fig. 2, both foils are wound together with a 2.5 x 220 mm separator 15 made of polyamide non-woven fabric, and adhesive tape 16 is applied to an end of this capacitor element. Re-anodization is implemented by immersing the capacitor element in 3% ammonium adipate solution, and  
 5 applying 70V at 70°C for 30 minutes. The capacitance of this wound aluminum electrolytic capacitor element is 55  $\mu$ F.

This capacitor element is impregnated with the conductive composition precursor prepared in Example 15, and then heated at 50 °C for 60 minutes and at 130 °C for 20 minutes to remove the medium and form the  
 10 conductive composition layer consisted of poly (3,4-ethylene dioxy thiophene) and fluorocarbon surface active agent. This is used as a base layer for the negative electrode conductive layer.

Then, 0.8 mol/l iron (II) salt of naphthalene sulfonic acid and 1.6 mol/l 3,4-ethylene dioxy thiophene monomer are mixed with methanol to prepare  
 15 polymerization solution. The capacitor element is immersed in this polymerization solution for application, then heated at 50 °C for 30 minutes and at 90 °C for 30 minutes, and cleaned and dried to form the conductive polymer layer made of the poly (3,4-ethylene dioxy thiophene). The negative electrode conductive layer consisted of the conductive composition  
 20 layer and conductive polymer layer is formed as described above.

Capacitance and electrical breakdown voltage of this capacitor are evaluated in the same way as that in Example 15. Table 1 shows the results.

#### (Comparative example 9)

25 For comparison, a capacitor without added fluorocarbon surface active agent to the conductive composition precursor which becomes a base layer is manufactured in Example 21 as Comparative example 9. The capacitance and electrical breakdown voltage of this capacitor are evaluated in the same way as in Example 15. Table 1 shows the results.  
 30 Comparative example 9 shows the poor coverage of the conductive composition layer because the fluorocarbon surface active agent is not added

to the conductive composition precursor. Moreover, the electrical breakdown voltage of the conductive composition layer is low because the fluorocarbon surface active agent which becomes an insulator after removing the medium is not added. Accordingly, as shown in Table 1, the electrical  
5 breakdown voltage of the capacitor is low and withstand characteristics are poor.

It is apparent from Comparative example 9 and Example 21 in Table 1 that Example 21 provides a capacitor with good withstand voltage by using the conductive composition layer with good withstand voltage and coverage as a  
10 base layer.

(Example 22)

Example 22 uses the same capacitor element as Example 21.

First, formation of the base layer is described. The capacitor element is  
15 immersed in the conductive composition precursor-manufactured in Example 18 and then heated at 50 °C for 60 minutes and at 130 °C for 20 minutes to remove the medium and form the conductive composition layer consisted of poly-aniline and fluorocarbon surface active agent. This is used as a base layer for the negative electrode conductive layer.

20 Then, the capacitor element is immersed in methanol solution at minus 30 °C containing 0.8 mol/l iron (II) salt of naphthalene sulfonic acid and 1.4 mol/l pyrrole monomer, and then cleaned and dried to form the conductive polymer layer made of the poly-pyrrole. The negative electrode conductive layer consisted of the base layer and conductive polymer layer is thus formed.  
25 The capacitance and electrical breakdown voltage of this capacitor are evaluated in the same way as that in Example 15. Table 1 shows the results.

(Comparative example 10)

For comparison, a capacitor without added fluorocarbon surface active  
30 agent to the conductive composition precursor which becomes a base layer is manufactured in Example 22 as Comparative example 10. The capacitance

and electrical breakdown voltage of this capacitor are evaluated in the same way as in Example 15. Table 1 shows the results.

Comparative example 10 shows the poor coverage of the conductive composition layer because the fluorocarbon surface active agent is not added to the conductive composition precursor. Moreover, the electrical breakdown voltage of the conductive composition layer is low because the fluorocarbon surface active agent which becomes an insulator after removing the medium is not added. Accordingly, as shown in Table 1, the electrical breakdown voltage of the capacitor is low and withstand characteristics are poor.

It is apparent from Comparative example 10 and Example 22 in Table 1 that the Example 22 provides a capacitor with good withstand voltage by using the conductive composition layer with good withstand voltage and coverage as a base layer.

(Example 23)

Example 23 further adds about 10 weight % of water soluble acrylic resin as a binder to the conductive composition precursor in Example 21. Other conditions are the same as those in Example 21 for manufacturing the capacitor.

The capacitance and withstand voltage are evaluated in the same way as Example 15. Table 1 shows the results. It is apparent from Table 1 that Example 23 has a higher withstand voltage than that in Comparative example 9, demonstrating the advantageous effect of the present invention.

The above examples refer to the case of using fluorocarbon surface active agents having the perfluoro alkyl group. Other fluorocarbon surface active agents of which a part of fluorine is substituted by hydrogen are also applicable to the present invention. In addition, several types of fluorocarbon surface active agents may be mixed for use. Furthermore, fluorocarbon surface active agent and hydrocarbon surface active agent may

be used together.

Examples related to the wound aluminum electrolytic capacitor refer to the use of polymerizing solution without containing fluorocarbon surface active agent or binder for the in-situ polymerization. However, fluorocarbon surface active agent or binder may be added to polymerizing solution for improving coverage or withstand voltage.

As described above, the addition of fluorocarbon surface active agent reduces surface tension, allowing to obtain conductive composition precursor with high coverage.

Moreover, addition of fluorocarbon surface active agent which becomes an insulator when the medium is removed, and further addition of binder, enable to provide conductive composition with high withstand voltage when the medium is removed from the conductive composition precursor.

#### (Example 24)

Example 24 is described with reference to Figs. 3A and 3B. Fig. 3A is a plan view and Fig. 3B is a sectional view of a capacitor element.

First, 1 mm width polyimide tape 2 is attached on both sides of 8 mm (L) x 3.3 mm (W) etched aluminum foil 1 in a way to partition the etched aluminum foil to 4mm and 3 mm portions. Then, positive electrode lead 7 is attached to the 3 mm x 3.3 mm portion of foil 1. Dielectric layer 3 is formed by anodizing the 4 mm x 3.3 mm portion of foil 1, using 3% ammonium adipate solution at 70 °C. As for anodizing conditions, the voltage is increased from 0V to 10V at the rate of 10 mV/s, and then the rated voltage of 10V is applied for 40 minutes. After rinsing under running deionized water for 10 minutes, the etched foil is dried at 105°C for 30 minutes. This structure is considered as a capacitor, and the capacitance in the anodizing solution is measured. The capacitance is 18  $\mu$ F.

Next, sulfonated polyaniline solution composition in which about 5 weight % of soluble conductive polymer is dissolved is prepared in accordance with the method disclosed in Synthetic Metals (Elsevier Press), 85,

pp 1397. The conductive composition precursor is prepared by adding 0.01 mol/l of tri-isopropyl naphthalene sulfonic acid to the sulfonated polyaniline solution composition.

Then, the conductive composition precursor is applied to the 4 mm x 3.3 mm portion of etched aluminum foil 1, and heated at 50 °C for 60 minutes and at 150 °C for 10 minutes to remove the medium and to form conductive composition layer 4 consisting of polyaniline and tri-propyl naphthalene sulfonic acid .

Next, conductive polymer layer 5 is formed on conductive composition layer 4 by chemical polymerization. First, monomer solution of 3,4-ethylene dioxy thiophene (EDOT) monomer is prepared. Oxidizing agent solution in which iron (II) salt of naphthalene sulfonic acid is dissolved in methanol is prepared. Then, the monomer solution and oxidizing agent solution are mixed to prepare the mixed solution. Here, the mixed solution is prepared to achieve the concentration of 1.6 mol/l EDOT and 0.8 mol/l iron (II) salt of naphthalene sulfonic acid. The portion of etched aluminum foil 1 where conductive composition layer 4 is formed is immersed in the mixed solution for 1 minute , and heated at 50°C for 30 minutes and at 100°C for 30 minutes to form conductive polymer layer 5 on conductive composition layer 4 by chemical polymerization.

Then, etched aluminum foil 1 is rinsed and dried. A process from immersion to drying is repeated for 10 times until a specified thickness is achieved for conductive polymer layer 5.

Then, collector layer 6 consisted of a carbon layer and silver paint layer is formed on conductive polymer layer 5, and negative electrode lead 8 is attached to collector layer 6.

After the attachment of the electrode lead 8, packaging with epoxy resin was performed, followed by aging to complete 10 capacitors in total.

For these 10 capacitors, the capacitance at 1 kHz, dissipation factor, impedance at 400 kHz, and leak current after applying the rated voltage of 6.3 V for 2 minutes are measured. In addition, loaded heat resistance and

moisture resistance tests by applying the rated voltage under the 85 °C and 85% RH are implemented to measure capacitance, loss coefficient, impedance, and leak current. Table 2 shows the results of mean values.

In the present Example, tri-isopropyl naphthalene sulfonic acid anion  
5 contained in the conductive composition layer suppress a damage in the dielectric layer caused by small volume naphthalene sulfonic acid. Accordingly, as shown in Table 2, the solid electrolytic capacitor with low leak current, and high heat and moisture resistance is obtained. In addition, the use of an oxidizing agent having small volume naphthalene sulfonic acid  
10 anion for chemical polymerization allows to provide the solid electrolytic capacitor with high capacitance obtaining rate, as shown in Table 2. Accordingly, the present invention offers the solid electrolytic capacitor with low leak current, high heat and moisture resistances, and high capacitance obtaining rate.

15

(Comparative example 10)

As for Comparative example 10, a conductive composition layer is directly formed on the dielectric layer, without providing a conductive composition layer as in Example 24, for manufacturing a capacitor. The conductive  
20 composition layer is formed in the same way as Example 24. Table 2 shows the results of measured characteristics. Leak current is high in Comparative example 10, as shown in Fig. 2, because the dielectric layer is damaged by naphthalene sulfonic acid anion, and characteristics degrade in the loaded heat resistance and moisture resistance tests, resulting in a capacitor with poor  
25 characteristics.

(Example 25)

Example 25 shows the effects of using aqueous dispersion composition containing poly (3,4-ethylene dioxy thiophene) particles, instead  
30 of sulfonated polyaniline solution composition for manufacturing the capacitor in Example 24.

How the conductive composition precursor is manufactured is described next. Aqueous dispersion composition containing about 0.4 weight % of colloidal poly (3,4-ethylene dioxy thiophene) particles is prepared in accordance with the method disclosed in Synthetic Metals (Elsevier Press),  
5 85, pp 1397. Then, 0.01 mol/l tri-isopropyl naphthalene sulfonic acid and 0.5 weight % alcoxy silane as a binder are added to the above aqueous dispersion composition for manufacturing the conductive composition precursor. A solid electrolytic capacitor is manufactured in the same way as Example 24, and evaluated. Table 2 shows the results.

10 Compared to Comparative example 10, Example 25 has lower leak current, higher heat resistance and moisture resistance, and higher capacitance obtaining rate, demonstrating the advantageous effect of the present invention.

(Example 26)

15 In Example 26 the surface of the etched aluminum foil is anodized in the same way as Example 24 at 70 °C using solution containing 0.05 mol/l ammonium salt of tri-isopropyl naphthalene sulfonic acid for forming the dielectric layer. The capacitance of the capacitor in the anodizing solution is 17.8  $\mu$ F.

20 Then, the conductive polymer layer is formed by chemical polymerization, in the same way as Example 24 on the dielectric layer, using EDOT as monomer and iron (II) salt of naphthalene sulfonic acid as an oxidizing agent.

25 Next, the collector layer consisted of the carbon layer and silver paint layer is formed on the conductive polymer layer, and the negative electrode lead is attached on the collector layer.

After packaging with epoxy resin, aging is applied to complete 10 capacitors in total. These capacitors are measured in the same way as those in Example 24. Table 2 shows the results.

30 Tri-isopropyl naphthalene sulfonic acid anion included or present near the surface of the dielectric layer by anodization suppresses a damage to the



dielectric layer in the present Example. Accordingly, as shown in Table 2, the solid electrolytic capacitor with low leak current and high heat and moisture resistances is obtained.

The use of an oxidizing agent containing small volume naphthalene sulfonic acid anion, as in the present Example, allows to provide the solid electrolytic capacitor with high capacitance obtaining rate, as shown in Table 2. Accordingly, the solid electrolytic capacitor with low leak current, high heat and moisture resistances, and high capacitance obtaining rate is obtained.

#### 10 (Example 27)

The surface of the etched aluminum foil is anodized in the same way as in Example 24 to form the dielectric layer. Then, the conductive polymer layer is formed by chemical polymerization, in the same way as in Example 24 on the dielectric layer, using EDOT as monomer and iron (II) salt of naphthalene sulfonic acid as an oxidizing agent.

Next, re-anodization is implemented using anodizing solution in which 0.01 mol/l tri-isopropyl naphthalene sulfonic acid is dissolved in ethylene glycol. More specifically, a portion of the etched aluminum foil where conductive polymer layer is formed is impregnated with the anodizing solution at 70 °C. The voltage is increased from 0V to 8.5V at the rate of 10 mV/s, and then the rated voltage of 8.5V are applied for 40 minutes for re-anodization. Then, rinsing and drying are implemented.

The collector layer consisted of the carbon layer and silver paint layer is formed on the conductive polymer layer, and then the negative electrode lead is attached.

After packaging with epoxy resin, aging is applied to complete 10 capacitors in total. These capacitors are measured in the same way as those in Example 24. Table 2 shows the results.

Tri-isopropyl naphthalene sulfonic acid anion used in Example 27 has high repairing ability, and thus no large current flows during re-anodization, preventing decomposition of the conductive polymer layer. Accordingly, the

solid electrolytic capacitor with low leak current, without degrading the dissipation factor or impedance, is obtained.

(Comparative example 11)

- 5 As for Comparative example, a capacitor is manufactured by re-anodization using 0.5 mol/l of ammonium adipate, instead of tri-isopropyl naphthalene sulfonic acid as seen in Example 27. Table 2 shows measuring results.

Since ammonium adipate in the capacitor of Comparative example 11 has low repairing ability, large current flows during re-anodization,  
10 decomposing the conductive polymer layer. It is apparent from Table 2 that the dissipation factor and impedance are high and leak current is also large.

The above Examples refer to the case of using tri-isopropyl naphthalene sulfonic acid anion as alkyl naphthalene sulfonic anion. Other anionic materials such as mono-isopropyl naphthalene sulfonic acid anion, n-  
15 butyl naphthalene sulfonic acid anion, di-butyl naphthalene sulfonic acid anion, and tri-isopropyl naphthalene di-sulfonic acid anion may also be used. The present invention is thus not limited to types of anion.

The above Examples also refer to the case of using iron (II) salt of naphthalene sulfonic acid as an oxidizing agent having small volume anion.  
20 Other substances such as iron (II) salt of benzene sulfonic acid, benzene di-sulfonic acid, ethyl benzene sulfonic acid, dodecyl benzene sulfonic acid, and para-toluene sulfonic acid are applicable. The present invention is thus not limited to types of compounds as long as small volume anion is contained.

The above Examples also refer to the case of using ammonium salt of  
25 tri-isopropyl naphthalene sulfonic acid and tri-isopropyl naphthalene sulfonic acid separately as electrolyte of the anodizing solution. However, these electrolytes may be mixed with other electrolytes such as adipic acid, boric acid, acetic acid, phosphoric acid, and their salts.

The above Examples refer to the use of EDOT as monomer and iron  
30 (II) salt of naphthalene sulfonic acid as an oxidizing agent, and the conductive polymer layer is formed by chemical polymerization. However, other

monomers and oxidizing agents are applicable. The present invention is thus not limited to types of monomers and oxidizing agents.

The above Examples also refer to the formation of the conductive composition layer by chemical polymerization. However, electro-  
5 polymerization may be applied after chemical polymerization to form laminated conductive polymer layers.

In the above Examples, only the use of flat etched aluminum foil is described. It is apparent, however, that the present invention is applicable to capacitors made of porous sintered body or those in which the positive  
10 electrode foil and negative electrode foil are wound through with the separator. The present invention is thus not limited by the shape of the electrode.

As described above, the use of alkyl naphthalene sulfonic acids or their salts contained in the conductive composition layer suppresses a damage to the dielectric layer caused by small volume anion such as para-toluene  
15 sulfonic acid anion and naphthalene sulfonic acid anion. Accordingly, the solid electrolytic capacitor with low leak current and high heat and moisture resistance is obtained. When an oxidizing agent having small volume anion such as para-toluene sulfonic acid anion and naphthalene sulfonic acid anion is used, the solid electrolytic capacitor with high capacitance obtaining rate is  
20 obtained. Accordingly, the present invention has an advantageous effect of manufacturing the solid electrolytic capacitor with low leak current, high heat and moisture resistances, and high capacitance obtaining rate.

Alkyl naphthalene sulfonic acid anion included or present near the surface of the dielectric layer by anodization in the present invention  
25 suppresses a damage to the dielectric layer, enabling the achievement of a solid electrolytic capacitor with low leak current and high heat and moisture resistances. The use of small volume anion such as para-toluene sulfonic acid anion and naphthalene sulfonic acid anion as an oxidizing agent also enables the achievement of a solid electrolytic capacitor with high capacitance  
30 obtaining rate.

### Second exemplary embodiment

In the second exemplary embodiment the anodized film surface of the solid electrolytic capacitor is treated with at least one selected from silane coupling agent, titanium coupling agent, borane coupling agent, and aluminum coupling agent. Further, a coupling agent layer and a layer made of surface active agent showing high affinity to this coupling agent are provided to prevent direct contact between the anodized film-defect portion and the conductive polymer for improving the withstand voltage.

In other words, the second exemplary embodiment provides a layer consisted of a coupling agent and surface active agent between an electrode on which an anodized film is formed and a negative electrode conductive layer made of conductive polymer.

Existence of an insulating layer consisted of coupling agent and surface active agent in the second exemplary embodiment also significantly improves leak current characteristics. Since the thickness of the coupling agent and surface active agent layer are extremely thin, there is no noticeable drop in the capacitance or increase in high frequency impedance by the insertion of the insulating layer. On contrary, the penetration of the coupling agent and surface active agent deep into an etching pit of positive electrode valve metal or sintered body allows to wet the electrode surface, increasing the capacitance of the capacitor by broadening an area covered with conductive polymer.

Fluorocarbon surface active agents in which hydrogen in the alkyl group are substituted with fluorine are preferable in this exemplary embodiment. These types of surface active agents have high permeability as well as high heat resistance. They also show high affinity to the coupling agent.

Coupling agents having the above functions are listed below:

Silane coupling agent: Vinyl tri-chloro silane, vinyl ( $\beta$ -methoxy silane), vinyl tri-ethoxy silane,  $\gamma$ -methachryloiloxy silane,  $\beta$ -(3,4-epoxy cyclohexyl) ethyl-tri-methoxy silane,  $\gamma$ -glycidyloxy propyl tri-methoxy silane,

N-β (amino ethyl) γ -amino propyl methoxy silane, γ -amino propyl tri-ethoxy silane, N-phenyl- γ -amino propyl methoxy silane, γ -mercapto propyl methoxy silane, and γ -chloro propyl tri-methoxysilane.

Titanium coupling agent: Iso-propyl tri-isostealol titanate, iso-propyl  
 5 tris (dioxyl pyrophosphite) titanate, iso-propyl tri (N-amino ethyl-amino ethyl) titanate, tetra-octyl bis (di-tridecyl phosphite) titanate, tetra (2,2-diaryl oxymethyl-1-butyl) bis (di-tridecyl) phosphite titanate, bis (di-octyl pyrophosphate) oxy acetate titanate, bis (dioctyl pyrophosphate) ethylene titanate, isopropyl tri-octanoyl-titanate, iso-propyl di-methacryl iso-stealol titanate,  
 10 isopropyl tri-dodecyl benzene sulfonyl titanate, isopropyl isostealol diacryl titanate, isopropyl tri (dioctyl phosphate) titanate, isopropyl tri-cumyl phenyl titanate, and tetra-isopropyl bis (dioctyl phosphite) titanate.

Aluminum coupling agent: Aceto alcoxyl aluminum di-iso propylate.

Other than these compounds, borane coupling agents are applicable.

15 As for surface active agents, nonionic surface active agents as well as anionic surface active agents are applicable. These surface active agents are listed below:

Anionic surface active agents: Fatty acid soap, sulfated oil, higher alcohol, sulfuric acid ester of olefin or alkyl ether, alkyl sulfonate, alkyl aryl  
 20 sulfonate, sulfo succinic acid ester, fatty acid amido sulfonate, alkyl phosphoric acid ester, and alkyl ether phosphoric acid ester.

Nonionic surface active agents: Alkyl ether, alkyl phenyl ether, alkyl phenyl ether condensate, alkyl ester, alkyl amine, alkyl amido, polyoxy propylene ether, condensed oil ether, aryl phenyl ether, glycerine fatty acid  
 25 ester, sorbitane fatty acid ester, poly-oxyethylene sorbitane fatty acid ester, alkanol amido, and polyether.

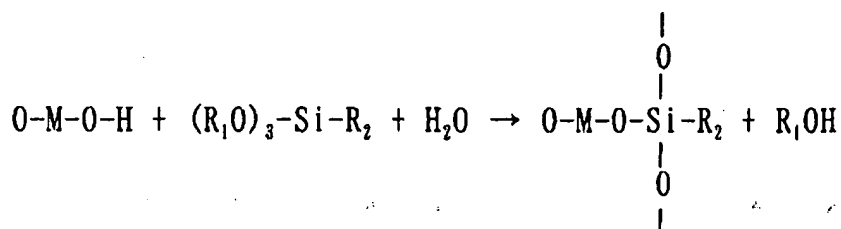
Surface active agents having the structure that hydrogen in the hydrophobic group is substituted with fluorine have high permeability, particularly preferable for wetting the electrode surface having fine surface  
 30 structure, and high heat resistance.

Fluorocarbon surface active agents having the molecular structure of

fluorine bound to carbon in the hydrophobic group are listed below.

Fluorocarbon surface active agent: perfluoro alkyl carbonate,  
perfluoro alkyl phosphoric acid ester, perfluoro alkyl tri-methyl ammonium,  
perfluoro alkyl betaine, perfluoro alkyl amine oxide, and perfluoro alkyl EO  
5 adducts.

The hydroxyl group exists on the anodized electrode surface, and the coupling agent, such as silane coupling agent described below, forms a strong organic layer by chemically reacting with the hydroxyl group.



M : metal atom

R<sub>1</sub>, R<sub>2</sub> : organic radical

10 Other coupling agents also form an extremely thin and strong organic film on an inorganic surface by the same structure. The present invention further forms the surface active agent layer on the coupling agent layer for preventing direct contact of the conductive polymer layer, formed on the surface active agent layer, and dielectric-layer defect portion. This allows to  
15 provide a capacitor with good leak current and withstand voltage characteristics.

The use of surface active agent also improves the wettability between the conductive polymer layer forming solution and coupling agent, increasing the coverage of the conductive polymer layer and capacitance obtaining rate.

20 The coupling agent layer is formed by impregnating a capacitor unit with the coupling agent solution using an appropriate solvent, and then evaporating the solvent.

The conductive polymer layer is formed by applying pre-polymerized

conductive polymer particles or soluble conductive polymer dispersed or dissolved in the medium containing a surface active agent, using an appropriate method.

Conductive polymer may also be formed by in-situ polymerization in a polymerizing medium containing monomer, oxidizing agent, and surface active agent for forming the negative electrode conductive layer.

The above combinations also allow to form the negative electrode conductive layer made of the conductive polymer layer. For the above purpose, conductive polymer having pyrrole, thiophene, aniline, or their derivatives as a repeating unit may be used.

As for thiophene derivatives, 3,4-ethylene dioxy thiophene may be used. As for aniline derivatives, sulfonated aniline may be used.

In-situ polymerization is applicable by electro-polymerization as well as chemical oxidative polymerization. Specific examples are described below with reference to Figs. 4 and 5.

#### (Example 28)

As shown in Fig. 4, a voltage of 35V is applied to electrode foil 11 made of a 8 x 20 mm etched aluminum foil to which positive electrode lead 10 of 0.5 aluminum is attached is etched, using 3% ammonium adipate solution at about 70 °C to form dielectric layer 12 made of an anodized film as shown in Fig. 5 for the positive electrode of the capacitor.

This electrode foil 11 is immersed in 1% solution of (A)  $\gamma$ -glycidoxy propyl trimethyl silane, (B)  $\gamma$ -methacryloxy propyl trimethoxysilane, and (C) N- $\beta$  (aminoethyl)  $\gamma$ -aminopropyl trimethoxy silane, and then air dried at 110 °C to form coupling agent layer 13.

These silane coupling agents are supplied by Shin Etsu Chemicals Industry in the trade name KBM403, KBM503, and KBM 603, which are easily available on the market.

Then, the above positive electrode is impregnated with the polypyrrole solution containing 0.1% perfluoro alkyl phosphoric acid ester, which is a

surface active agent, and air dried. The surface active agent whose hydrogen in the alkyl group is substituted with fluorine is supplied by Asahi Glass Co., Ltd. in the trade name Surflon, and is easily available on the market. The surface active agent used in Example 28 is Surflon S112.

- 5           The polypyrrole solution is prepared in accordance with a method disclosed by E.E. Havinga et al, Chemistry of Materials (American Chemical Society), 1 (6), pp650 (1989).

          The immersion and air-dry processes are repeated until electrode foil 11 is completely covered to form surface active agent layer 14 and conductive  
10   polymer layer 15.

          Colloidal graphite and silver paint are then applied sequentially to form graphite layer 16 and silver paint layer 17, completing five capacitors with a sectional structure shown in Fig. 5.

- The capacitance,  $\tan \delta$  at 1 kHz and leak current after applying 13V  
15   for 2 minutes are measured. Table 3 shows mean values of the measurements. The withstand voltage when a voltage in the forward direction is applied at the voltage raising speed of 40 mV/sec is 24V, 25V, and 23V respectively for (A), (B), and (C).

- 20           (Comparative example 12)

          As for comparison, five capacitors without treatment of (A) Silane coupling agent KBM403 and five capacitors with no additive of (B) Surflon S112 are manufactured in Example 28 as Comparative example 12. The capacitance,  $\tan \delta$ , and leak current are evaluated in the same way as  
25   Example 28. Table 3 shows the results. Withstand voltage of (A) and (B) in Comparative example 12 are 16V and 18V respectively.

          Comparing the results shown in Table 3, high leak current is noticed when no silane coupling agent treatment is applied, and only a capacitor with small capacitance is obtained without fluorocarbon surface active agent.

- 30           In other words, it can be assumed that a thin layer of silane coupling agent and fluorocarbon surface active agent acts as an insulating layer to



reduce leak current and increase withstand voltage. In addition, the fluorocarbon surface active agent improves the wettability between the silane coupling agent layer and polypyrrole solution, increasing the capacitance and reducing  $\tan \delta$  of the capacitor by improved coverage.

5

(Example 29)

Example 29 shows the effects of using (A) Surflon S111 (salt of perfluoro carboxylic acid) and (B) Surflon S141 (perfluoro alkyl amine oxide), instead of Surflon S112 as seen in Example 28 after treating with the silane  
10 coupling agent KBM 403. Five capacitors are manufactured with (A) and (B) respectively for evaluation.

Table 3 shows the results. It is apparent that all the capacitors in Example 29 have a higher capacitance, good  $\tan \delta$ , and good leak current characteristics than that in Comparative example 12, demonstrating the  
15 advantageous effect of the present invention.

(Example 30)

Example 30 shows the effects of using titanium coupling agents (A) isopropyl tri-isostearoil titanate and (B) tetraoctyl bis (di-tridecyl phosphate)  
20 titanate, and aluminum coupling agent: (C) acetoalcoxyl aluminum di-isopropylate, instead of the silane coupling agent as seen in Example 28. Five capacitors are manufactured with (A), (B), and (C) respectively for evaluation.

The above titanium and aluminum coupling agents are supplied by Ajinomoto K.K. in the trade name of Plainact TTS, Plainact 46B, and Plainact  
25 AL-M, which are easily available on the market.

Table 3 shows evaluation results of the capacitors. It is apparent that all the capacitors in Example 30 have a higher capacitance, good  $\tan \delta$ , and good leak current characteristics than those in Comparative example 12, demonstrating the advantageous effect of the present invention.

30

(Example 31)

Example 32 shows the effects of using 0.4% colloidal polyethylene di-oxy thiophene particle dispersion, instead of the poly-pyrrole solution as seen in Example 28

Capacitors are evaluated in the same way as Example 28. Table 3 shows the results. It is apparent that all the capacitors in Example 31 have a higher capacitance, better  $\tan \delta$ , and better leak current characteristics than those in Comparative example 12, demonstrating the advantageous effect of the present invention.

(Example 32)

Example 32 shows the effects of immersing the foil in the dispersion once, instead of repeatedly immersing in the colloidal polyethylene di-oxy thiophene dispersion as seen in Example 31, for forming the negative electrode conductive layer, and the polyethylene dioxy thiophene layer is laminated by in-situ chemical polymerization. Other conditions are the same as those in Example 28 for preparing five capacitors.

The capacitor element is impregnated with methanol solution containing 1.9M ethylene di-oxy thiophene monomer and 1.1M iron (II) salt of para-toluene sulfonic acid once and then heated at 45 °C and 85 °C for 1 hour each for in-situ polymerization of polyethylene dioxy thiophene. After polymerization, the capacitor element is rinsed with methanol and water to remove polymerization residue.

Capacitors are evaluated in the same way as Example 28.

Table 3 shows the results. It is apparent that all the capacitors in Example 33 have a higher capacitance, better  $\tan \delta$ , and better leak current characteristics than that in Comparative example 12, demonstrating the advantageous effect of the present invention.

(Example 33)

Example 33 uses 1% poly-aniline aqueous solution. Water solubility is given to the polymer by introducing the sulfone group to the aniline

structure.

Example 33 shows the effects of using the poly-aniline solution, instead of colloidal polyethylene dioxy thiophene solution as seen in Example 32, for forming five capacitors, and they are evaluated. Table 3 shows the results. It is apparent that all the capacitors in Example 33 have a higher capacitance, better  $\tan \delta$ , and better leak current characteristics than that in Comparative example 12, demonstrating the advantageous effect of the present invention.

#### 10 (Example 34)

Example 34 shows the effects of laminating poly-pyrrole layers by in-situ polymerization, instead of polyethylene dioxy thiophene layers by in-situ polymerization as seen in Example 32, for forming five capacitors.

The capacitor element is immersed alternatively in the monomer solution containing 0.75M pyrrole monomer, 0.04M sodium salt of tri-isopropyl naphthalene sulfonic acid and 0.1 weight % Surflon S112; and the oxidizing agent solution containing 0.4M ferrous sulfate and 0.1 weight % Surflon S12 for in-situ polymerization of polypyrrole. The conductive polymer is polymerized at room temperature for 1 hour.

20 Table 3 shows the evaluation of the capacitors. It is apparent that all the capacitors in Example 34 have a higher capacitance, better  $\tan \delta$ , and better leak current characteristics than that in Comparative example 12, demonstrating the advantageous effect of the present invention.

#### 25 (Example 35)

Example 35 shows the effects of using an embossed tantalum foil of 99.99% purity and the same dimensions, instead of the aluminum strip as seen in Example 28. A tantalum lead of 0.5 mm diameter is welded to this tantalum foil. After forming the anodized film on the tantalum foil by applying 35V for 1 hour using 0.5% phosphoric acid solution at 90 °C, capacitors are manufactured in the same way as Example 32. Table 3 shows

the results of evaluation. Measured withstand voltage is 28V.

(Comparative example 13)

For comparison, five capacitors without (A) treatment with silane  
 5 coupling agent KBM 403 in Example 32 and without (B) addition of Surflon  
 S112 in Example 35 are manufactured as Comparative example 13.

Capacitance,  $\tan \delta$ , and leak current are evaluated, and the results are  
 shown in Table 3. Measured withstand voltage is 22V for (A) and 24V for  
 (B).

10 It is apparent from Table 3 that capacitors without silane coupling  
 agent treatment show large leak current, and those without using fluorocarbon  
 surface active agent show small capacitance.

Capacitors of Examples of the present invention thus have larger  
 capacitance, better  $\tan \delta$  and leak current characteristics, and higher withstand  
 15 voltage, demonstrating that the present invention has better effect.

Examples of the present invention only refer to the foil structure of the  
 valve metal electrode. However, elements which have a structure to wind the  
 negative electrode foil and positive electrode foil together with the separator  
 in advance are also applicable, and porous sintered elements made of fine  
 20 valve metal powder are further applicable. The present invention is thus not  
 limited to electrode structures.

The above Examples only refer to the use of aluminum or tantalum as  
 valve metals. However, other valve metals such as titanium, zirconium, and  
 niobium are applicable.

25 The above Examples only refer to the structure of surface active agent  
 whose hydrogen in the hydrophobic group is all substituted with fluorine.  
 However, those having high wettability even with remaining hydrogen are  
 also applicable.

In case of thiophene and aniline conductive polymers, the above  
 30 Examples only refer to those having one type of substitute group. However,  
 as long as conductivity is sufficiently high, those having other substitute

groups are also applicable. Conductive polymers with other structure may also be applied.

The above Examples only refer to methods for forming the conductive polymer layer using conductive polymer dispersion or solution independently  
5 or further laminating conductive polymer by in-situ polymerization after the formation of the conductive polymer layer.

However, the conductive polymer layer may also be formed only by in-situ polymerization. The present invention is thus not limited to the conductive polymer layer formation methods.

10 The above examples only refer to chemical polymerization as a method for forming conductive polymer by in-situ polymerization. However, it is apparent that electro-polymerization is also applicable.

Examples of the present invention enables to provide a solid electrolytic capacitor with good leak current characteristics and high withstand  
15 voltage by the formation of extremely thin insulating layer on the dielectric surface.

In addition, the use of fluorocarbon surface active agent having high wettability in conductive polymer dispersion or in in-situ polymerization medium enables to significantly improve the coverage and adhesion of  
20 conductive polymer, and achieve a significant effect of obtaining a capacitor with high capacitance obtaining rate and small  $\tan \delta$ .